Supporting Information

Computational Screening of Single-Atom Alloy TM@Ru(0001) for Enhanced Electrochemical Nitrogen Reduction Reaction

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Details of Micro-kinetic simulations

The following are the various elementary steps involved during the N_2 reduction via consecutive mechanism

$N_2 + * = *N_2$ (E1)

$H_2 + 2* = 2H*$ (E2)

$*N_2 + *H = *NNH + *$ (E3)

$*NNH + *H = *NNH_2 + *$ (E4)

$*NNH_2 + *H = *N + *NH_3$ (E5)

$*N + *H = *NH + *$ (E6)

$*NH + *H = *NH_2 + *$ (E7)

$*NH_2 + *H = *NH_3$ (E8)

$*NH_3 = NH_3 + *$ (E9)

* Represents a reaction site

The set of rate and equilibrium equations considered in the kinetic model are as follows:

$$\theta_{*N_2} = K_1 p_{N2} \theta_v \quad (1)$$

$$\theta_{*H} = \sqrt{K_2 P_{H_2} \theta_v} \quad (2)$$

$$r_3 = \vec{k}_3 \theta_{*N_2} \theta_{*H} - \overleftarrow{k}_3 \theta_{*NNH} \theta_v \quad (3)$$

$$r_4 = \vec{k}_4 \theta_{*NNH} \theta_{*H} - \overleftarrow{k}_4 \theta_{*NNH_2} \theta_v \quad (4)$$

$$r_5 = \vec{k}_5 \theta_{*NNH_2} \theta_{*H} - \overleftarrow{k}_5 \theta_{*N} \theta_{*NH_3} \theta_v \quad (5)$$

$$r_6 = \vec{k}_6 \theta_{*N} \theta_{*H} - \overleftarrow{k}_6 \theta_{*NH} \theta_v \quad (6)$$

$$r_7 = \vec{k}_7 \theta_{*NH} \theta_{*H} - \overleftarrow{k}_7 \theta_{*NH_2} \theta_v \quad (7)$$

$$r_8 = \vec{k}_8 \theta_{*NH_2} \theta_{*H} - \overleftarrow{k}_8 \theta_{*NH_3} \theta_v \qquad (8)$$

$$\theta_{*NH_3} = \frac{p_{NH_3} \theta_v}{K_9} \qquad (9)$$

k_i are the rate constants assumed to be of the Arrhenius form, K_i are the adsorption or desorption equilibrium constants, θ_v is the free active sites, θ_{*M} is the coverage of the species, *M, p is the gas partial pressure. The ammonia conversion factor is assumed to be 0.1. The reaction rate for the N_2 adsorption and ammonia desorption can be given by the equation $k_i = A_i^* exp^{(-\frac{G_{a,i}}{k_B T})}$, where $G_{a,i}$ stands for the activation free energy of the reaction, A_i^* is an effective pre-exponential factor given by $A_i^* = x\frac{k_B T}{h}$, where x is the effective coefficient, T is the temperature, k_B is the Boltzmann constant, h is the Plank constant.

The equilibrium constant can be given by the equation as follows

$$K_i = exp^{-\frac{\Delta G_i}{k_B T}}$$

In which, ΔG_i is the free energy change for N_2 adsorption and NH_3 desorption step.

Furthermore, the reaction rate for the electrochemical steps such as E3-E8 while taking electrode potential into consideration can be given by

$$\vec{k}_i = A_i exp^{\left(-\frac{E_{a,i}}{k_B T}\right)} \quad exp^{(-\frac{e\beta_i(U - U_i)}{k_B T})}$$

Where $E_{a,i}$ represents the activation barrier which can be calculated by CI-NEB method, $U_i = \frac{-\Delta G_i}{e}$ and β_i accounts for the symmetric factor which is taken equal to 0.50. Also, the equilibrium constant Ki for the electrochemical step can be written as $K_i = exp^{(-\frac{eU + \Delta G_i}{k_B T})}$. Thus, the $\overleftarrow{k}_i$, the reverse rate constant can be derived from the forward rate constant and equilibrium constant as follows

$$\overleftarrow{k}_i = \frac{K_i}{\vec{k}_i}$$

As E3 is only rate limiting step, all other hydrogenation steps are in equilibrium, therefore,

$r_4=r_5=r_6=r_7=r_8=0$.

Moreover, based on conversion law, the sum of coverage of all the reaction species equals to one. Thus,

$$\theta_{*N_2} + \theta_{*H} + \theta_{*NNH} + \theta_{*NNH_2} + \theta_{*N} + \theta_{*NH} + \theta_{*NH_2} + \theta_{*NH_3} + \theta_{*NH_3} + \theta_v = 1 \quad (10)$$

The free active site can be obtained as θ_v

$$\theta_v = 1/(1 + K_1 pN_2 + \sqrt{K_2 pH_2} + \frac{\vec{k}_4 \vec{k}_5 \vec{k}_6 \vec{k}_7 \vec{k}_8 p_{NH3}^2}{\vec{k}_4\, \vec{k}_5\, \vec{k}_6\, \vec{k}_7\, \vec{k}_8\, K_9^2 (K_2 pH_2)^{\frac{5}{2}}} + \frac{}{\vec{k}_5\, \vec{k}_6\, \vec{k}_7}$$

$$\vec{k}_6\, \vec{k}_7\, \vec{k}_8 \frac{p_{NH_3}^2}{\vec{k}_6} \vec{k}_7\, \vec{k}_8\, K_9^2 (K_2 pH_2)^{\frac{3}{2}} + \vec{k}_7 \frac{\vec{k}_8 p_{NH_3}^2}{\vec{k}_7\, \vec{k}_8 (K_2 pH_2)} + \frac{\vec{k}_8 p_{NH_3}}{\vec{k}_8\, K_9 \sqrt{K_2 pH_2}} +$$

$$K_9$$

$$= 1/(1 + K_1 pN_2 + \sqrt{K_2 pH_2} + \frac{p_{NH3}^2}{K_4 K_5 K_6 K_7 K_8\, K_9^2 (K_2 pH_2)^{\frac{5}{2}}} + \frac{p_{NH3}^2}{K_5 K_6 K_7 K_8\, K_9^2\, (K_2 pH_2)^2}$$

$$+ p_{NH3}^2 / K_6 K_7 K_8\, K_9^2 (K_2 pH_2)^{\frac{3}{2}} + \frac{p_{NH_3}^2}{K_7 K_8\, K_9^2 (K_2 pH_2)} + \frac{p_{NH_3}}{K_8\, K_9 \sqrt{K_2 pH_2}} + \frac{p_{NH_3}}{K_9} \quad (11)$$

Using the values of various parameters in the above equation to calculate the free active site θ_v, all the terms except $K_1 pN_2 + \sqrt{K_2 pH_2}$ and $\frac{p_{NH_3}}{K_9}$ are very small and thus can be neglected. Thus, the reaction rate r_3 can be calculated by using the above obtained value of θ_v in equation (3) as follows.

$$r_3 = \vec{k}_3 \theta_{*N_2} \theta_{*H} - \overleftarrow{k}_3 \theta_{*NNH} \theta_v$$

$$= \vec{k}_3 K_1 pN_2 \sqrt{K_2 pH_2} \theta_v^2 - \overleftarrow{k}_3 p_{NH3}^2 / K_4 K_5 K_6 K_7 K_8\, K_9^2 (K_2 pH_2)$$

The reverse reaction rate can be neglected as compared to the forward reaction rate, the value of θ_v can be used to obtain the value of turnover frequency.

Table S1: Free energy of hydrogen adsorption on the surface of the TM@Ru(0001) catalyst.

Catalyst, TM@Ru(0001)	ΔG (eV)
V@Ru(0001)	-1.15
Ti@Ru(0001)	-0.99

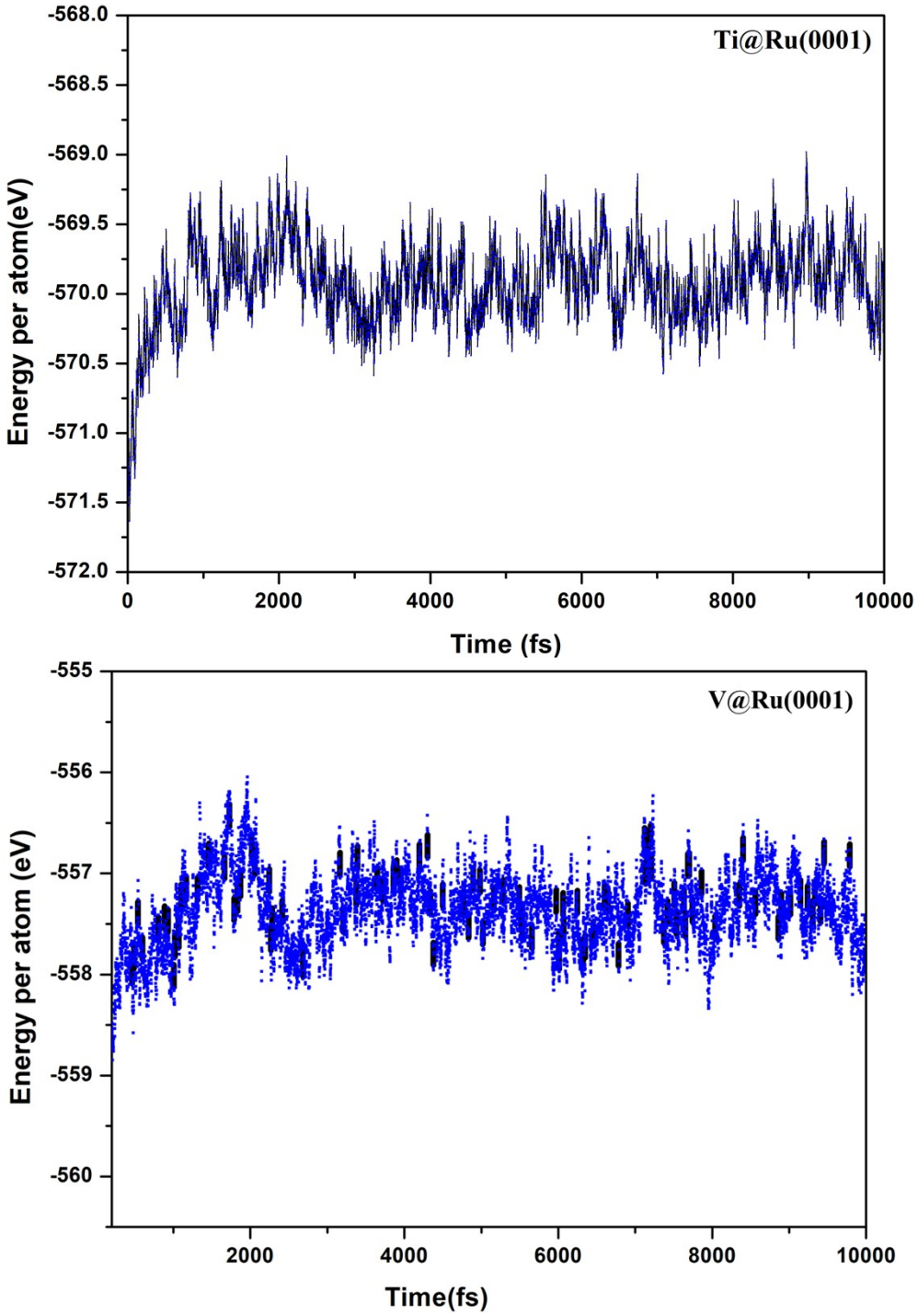


Figure S1: Variation of the energy per atom with the time for AIMD simulations for V@Ru(0001) and Ti@Ru(0001) complexes. The simulation run under 400K for 10ps with a time step of 1 fs.

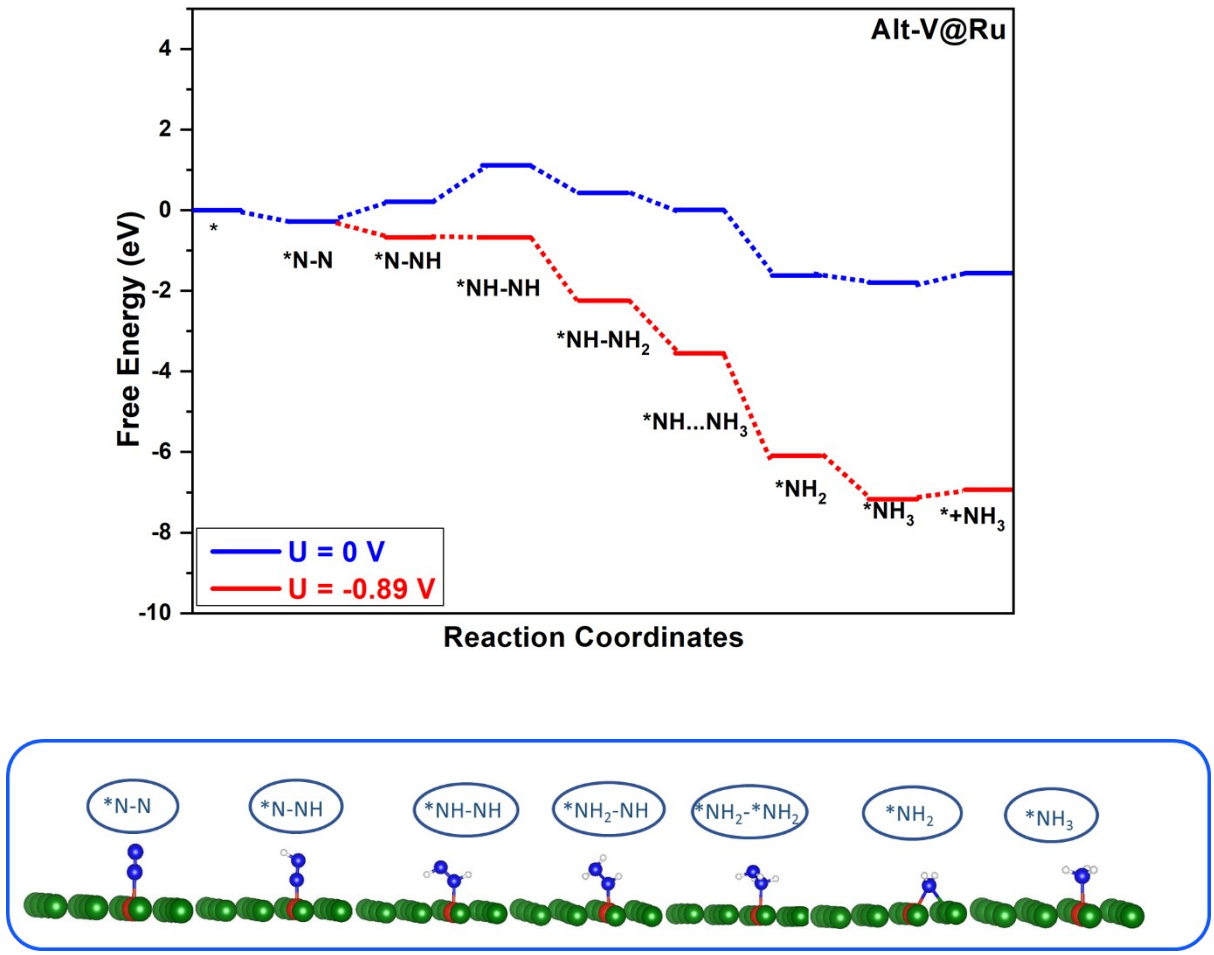
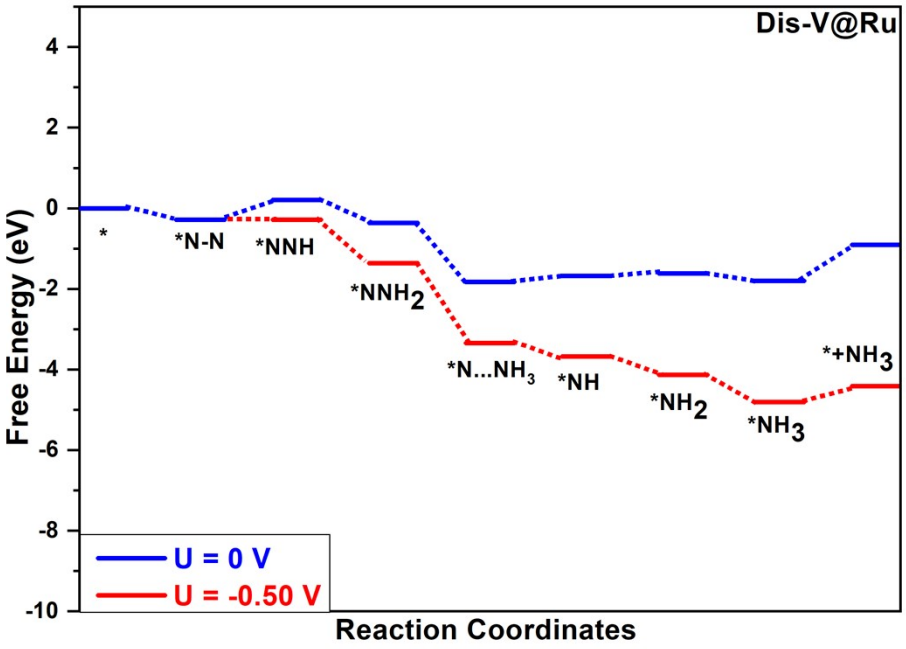


Figure S2: The free energy diagram for the conversion of N_2 to NH_3 using V@Ru(0001) following alternating reaction pathway. The optimized structures of the involved intermediates are shown at the bottom of the figure.



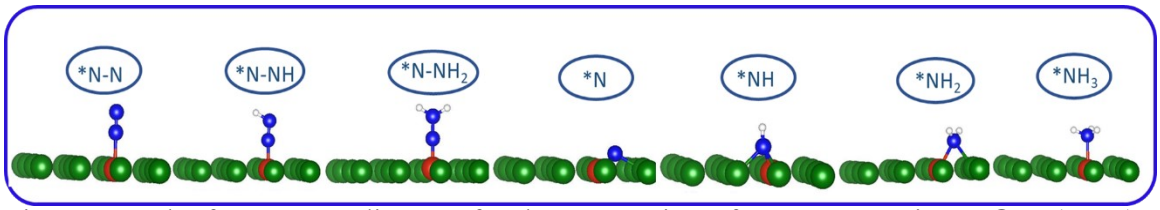


Figure S3: The free energy diagram for the conversion of N_2 to NH_3 using V@Ru(0001) following Distal reaction pathway. The optimized structures of the involved intermediates are shown at the bottom of the figure.

Table S2: Cartisian Coordinates of all the intermediates formed during the nitrogen reduction using V@Ru(0001).

*N-N

0.5225221242768356	0.5243587768122839	0.4115527964915471
0.4039276761358382	0.5267962871172462	0.4133922057785407
0.4190735657728194	0.5895929224707540	0.3188994349979279
0.0909643938894545	0.1704794515828789	0.0026255237242704
0.0807005346776807	0.1666694829256093	0.2170992451710851
0.1643029536953447	0.0815547680803528	0.1077256081193058
0.1691490929063882	0.0867238963076849	0.3229679834503817
0.3275549191417381	0.1682721887494521	0.0022292326690223
0.3329851305145872	0.1660825513578490	0.2179971142399948
0.4180400623737795	0.0840565266021342	0.1080034213047905
0.4086682882434208	0.0791049903154300	0.3236295158921409
0.5821344747770871	0.1682530519538378	0.0019242337900087
0.5832784266205411	0.1676411006515030	0.2186422980810225

0.6661655501712918 0.0858740379516447 0.1083525063081905
0.6642137110823049 0.0779353086532975 0.3236256889961289
0.8303661752449225 0.1697240288898821 0.0022034545529121
0.8323141028727987 0.1657627634496472 0.2178045379179534
0.9149211875327481 0.0845190360417744 0.1068105181828824
0.9158471719716624 0.0797235100442000 0.3237684611254752
0.0755283143167035 0.4143119755716217 0.0032127099615179
0.0843029767212708 0.4171415361692163 0.2179365841001520
0.1684422206422599 0.3350384712549334 0.1074985161492738
0.1618544278622805 0.3266280025801162 0.3230665431441083
0.3332927867639644 0.4114988766979804 0.0028576575593742
0.3323788497010540 0.4185812815325745 0.2200846644805161
0.4166123654527311 0.3358384368128456 0.1085304525135782
0.4083245599247212 0.3221037523472715 0.3224625097348891
0.5809761666507496 0.4123586673407207 0.0030791529122819
0.5837627754402609 0.4185905352015971 0.2185082203373561
0.6639622154019056 0.3318182499470628 0.1088142188712475
0.6698477884407354 0.3371134796644547 0.3241265523991768
0.8407459235801472 0.4223633496031606 0.0023323110057635
0.8303387905425299 0.4144430405010348 0.2182769413419220
0.9149970167103237 0.3317111068517573 0.1081185181868632
0.9204288377240025 0.3417462643307543 0.3240007589442992
0.0764610281754799 0.6596691162520517 0.0024375136902433
0.0838727264003220 0.6677609499059873 0.2175708890383543
0.1670641006048806 0.5834686285030299 0.1076369260113555
0.1595063053786065 0.5821404124525283 0.3230968856843568
0.3382069568632749 0.6728082479107399 0.0026778204677210
0.3330761154086134 0.6672457762939428 0.2185567358343633
0.4152933423016823 0.5838396947911687 0.1092052975968542
0.5850190308218174 0.6755589700231115 0.0025184633359000
0.5813104721841242 0.6646447961710367 0.2200847899567699
0.6648591836696197 0.5822401421476325 0.1077974544555831
0.6720556456369544 0.5871825552515275 0.3265064170941051
0.8320147471450718 0.6636095002406586 0.0026022677822231
0.8312691404728375 0.6678701198829988 0.2179935909474868
0.9160469963900186 0.5847629007816879 0.1081336345697125
0.9158415525164477 0.5745449721897544 0.3236840584062461
0.0869301361984298 0.9216948565697968 0.0021358063063418
0.0802872167069847 0.9135295993026278 0.2176419842532482
0.1671811215245144 0.8342126989236894 0.1064733770157575
0.1686065192230583 0.8327085544174023 0.3227506950157836
0.3376320745155676 0.9222546549818246 0.0028025196920547
0.3315430248131124 0.9162981646642130 0.2176616427282575
0.4140962495671414 0.8318688251417176 0.1072765166872918
0.4201685535791346 0.8373595636866461 0.3234662628369550
0.5820438930666543 0.9101459591495603 0.0026199563739965
0.5812868894854272 0.9185151308856472 0.2181635989999165
0.6670008081264039 0.8324929920608400 0.1077421239914048
0.6683805620899766 0.8409541431142681 0.3224371239672625

0.8262602996495341	0.9133396404421545	0.0021820085612454
0.8357166996069317	0.9178089490075760	0.2173596196807102
0.9161549140580768	0.8334307231010153	0.1068006142878327
0.9132680870424169	0.8359585773885824	0.3236830182947515

*N-*NH

0.4372171629549010	0.5987132194626500	0.4709375477496303
0.5795929905718201	0.5756343114196055	0.4171491061506085
0.4711543501953792	0.5960994435451342	0.4220604409547788
0.4129487916705038	0.5862279884769431	0.3222419941284014
0.0823403455506291	0.1683511949507988	0.0025463828075205
0.0831204160074751	0.1679743335385234	0.2171115064040607
0.1663014657466055	0.0823121984202131	0.1075111670355329
0.1633986807636188	0.0881625993794224	0.3213591284014674
0.3347600564722036	0.1720781961746242	0.0022685462698793
0.3325265594066633	0.1643275481970251	0.2179338198758582
0.4170462808948499	0.0835858106042466	0.1065893450478906
0.4239076069239686	0.0848693747797709	0.3233033535282150
0.5835496542444922	0.1719437346570321	0.0019849107569095
0.5835505958994313	0.1657449075563835	0.2177405486062174
0.6659048662330870	0.0834324050178673	0.1071915005678454
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0.8336935536285328	0.1686723478143392	0.2170041430332168
0.9152515334338218	0.0836274437635025	0.1075112728022320
0.9199401058980108	0.0800517772584298	0.3229538519019373
0.0897011726326864	0.4191978766429619	0.0022332552785828
0.0826524574167448	0.4152390965736984	0.2172026447429033
0.1686857552738827	0.3352815190789433	0.1073051912974447
0.1611378129329011	0.3296914347512546	0.3232979995726858
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0.3324105385778938	0.4180901041895658	0.2188721994107705
0.4157094941088073	0.3340214148799361	0.1081435810244267
0.4170193802531160	0.3251750354978462	0.3219660286844776
0.5868793662948547	0.4133145502923379	0.0025028351401062
0.5848000678322889	0.4180588943122918	0.2169515469049747
0.6668203296001485	0.3326051423458300	0.1075591687114951
0.6630719616110339	0.3344181787720348	0.3236145685800281
0.8282858848838891	0.4206033452962386	0.0017286697063697
0.8336547569503145	0.4158111334546636	0.2169099574867583
0.9159580726109394	0.3332348734271672	0.1067621382991901
0.9222966407919163	0.3393609683155083	0.3231707357462728
0.0888642798414414	0.6688945351961856	0.0022230087808321
0.0819601445197526	0.6677947172048563	0.2173293790337348
0.1675208493475616	0.5839721553180055	0.1075724682008647
0.1609455942319967	0.5837043902472158	0.3225381718113374
0.3282315616263016	0.6687532126000920	0.0013296044397842

0.3358900712032115	0.6668150775280771	0.2186334508376257
0.4172336030214683	0.5831625955054073	0.1085868953450287
0.5888359255572109	0.6714923677512419	0.0026529567422804
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0.6664269572047048	0.5846787633775904	0.1080812924581505
0.6618806244547167	0.5791392031354845	0.3306838029473840
0.8282230876555896	0.6622710893497594	0.0014265406070701
0.8330568415521353	0.6667939328307234	0.2165024367186263
0.9156221481364253	0.5830877777451172	0.1070245336491856
0.9153721428169782	0.5777885929366264	0.3228295809455990
0.0833262937411905	0.9179458790341749	0.0026676544612167
0.0830405234449177	0.9161500098495468	0.2182318950356229
0.1669074707915954	0.8350201659028080	0.1066388211799320
0.1676984323762125	0.8276026586865068	0.3223312172956653
0.3295154818629615	0.9101206004622212	0.0019564983577720
0.3334412761292597	0.9167224214531904	0.2179682237312336
0.4150739236194355	0.8333617085925259	0.1071985617448962
0.4167513375934147	0.8351088824495432	0.3234942923413094
0.5850580394162299	0.9127345304450307	0.0023690082894020
0.5830538184209691	0.9170364682990878	0.2176291207434205
0.6644968534470417	0.8307231845800935	0.1079252560885614
0.6704486918511007	0.8416553266337916	0.3222236094747798
0.8301054116988100	0.9196760647387031	0.0021240491645665
0.8342911430508101	0.9152843540951673	0.2174041633034590
0.9173347586297035	0.8335788850500409	0.1070967023954894
0.9140899480666952	0.8373629469085984	0.3231755040470254

*N-NH2

0.5558760041413043	0.5290744531833582	0.4584141223275178
0.7116246657313801	0.6961768029454681	0.4584659401974792
0.6306764570545736	0.6153480489975047	0.4303275370267737
0.5684703356825891	0.6649722421296391	0.3819469121342189
0.3990105050447376	0.5739772129810734	0.3217550900077032
0.0833340000000007	0.1666700000000034	0.0031000000000034
0.0832268560161627	0.1660816596304290	0.2168453343519191
0.1666590000000028	0.0833319999999986	0.1072180000000031
0.1655047244408926	0.0899943608636399	0.3223006163342138
0.3333330000000032	0.1666680000000014	0.0031090000000020
0.3346189258087970	0.1671735458013330	0.2169655335729233
0.4166680000000014	0.0833319999999986	0.1072180000000031
0.4282501137531022	0.0892115595008403	0.3235427472324495
0.5833340000000007	0.1666700000000034	0.0031000000000034
0.5849372334756933	0.1670394036976033	0.2178174114405023
0.6666590000000028	0.0833319999999986	0.1072180000000031
0.6608567910357345	0.0779019177086872	0.3234759920626010
0.8333330000000032	0.1666669999999968	0.0031090000000020
0.8356155573136453	0.1686055367658116	0.2168007155682937

0.9166680000000014	0.0833319999999986	0.1072180000000031
0.9192576434271915	0.0798693128716345	0.3239942364269247
0.0833340000000007	0.4166659999999993	0.0031000000000034
0.0830410936771943	0.4158068493116513	0.2174244766002588
0.1666650000000018	0.3333349999999982	0.1072190000000006
0.1655589027498688	0.3319858010218134	0.3235931437345022
0.3333299999999966	0.4166659999999993	0.0031000000000034
0.3347570035808062	0.4172113409801248	0.2178821446112653
0.4166680000000014	0.3333409999999972	0.1072180000000031
0.4145462224296990	0.3229566006414825	0.3227083221882186
0.5833340000000007	0.4166669999999968	0.0031000000000034
0.5839117318793854	0.4179483390938207	0.2176497702768550
0.6666650000000018	0.3333349999999982	0.1072190000000006
0.6611672259833642	0.3300547605771378	0.3226693923674578
0.8333310000000012	0.4166659999999993	0.0031000000000034
0.8356812246270463	0.4161828127141999	0.2166726124502350
0.9166680000000014	0.3333409999999972	0.1072180000000031
0.9241141330310879	0.3375765035950636	0.3246983383126392
0.0833330000000032	0.6666689999999988	0.0031000000000034
0.0827414997892672	0.6661899667708114	0.2172845371742656
0.1666590000000028	0.5833319999999986	0.1072180000000031
0.1639775173672307	0.5816626873443708	0.3233544688839748
0.3333330000000032	0.6666669999999968	0.0031090000000020
0.3350706980899750	0.6672065152079631	0.2179032958960051
0.4166680000000014	0.5833319999999986	0.1072180000000031
0.5833340000000007	0.6666689999999988	0.0031000000000034
0.5832935664345309	0.6667732037159816	0.2186444073136219
0.6666590000000028	0.5833319999999986	0.1072180000000031
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0.5833340000000007	0.4166669999999968	0.0031000000000034
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0.1666590000000028	0.5833319999999986	0.1072180000000031
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*NH-NH2

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0.9138000874418364	0.0884918839012439	0.3234299155686623
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0.1666650000000018	0.3333349999999982	0.1072190000000006
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0.9146109526971202	0.8313777988522186	0.3222504016062859

*NH2-*NH2

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0.3333330000000032	0.1666680000000014	0.0031090000000020
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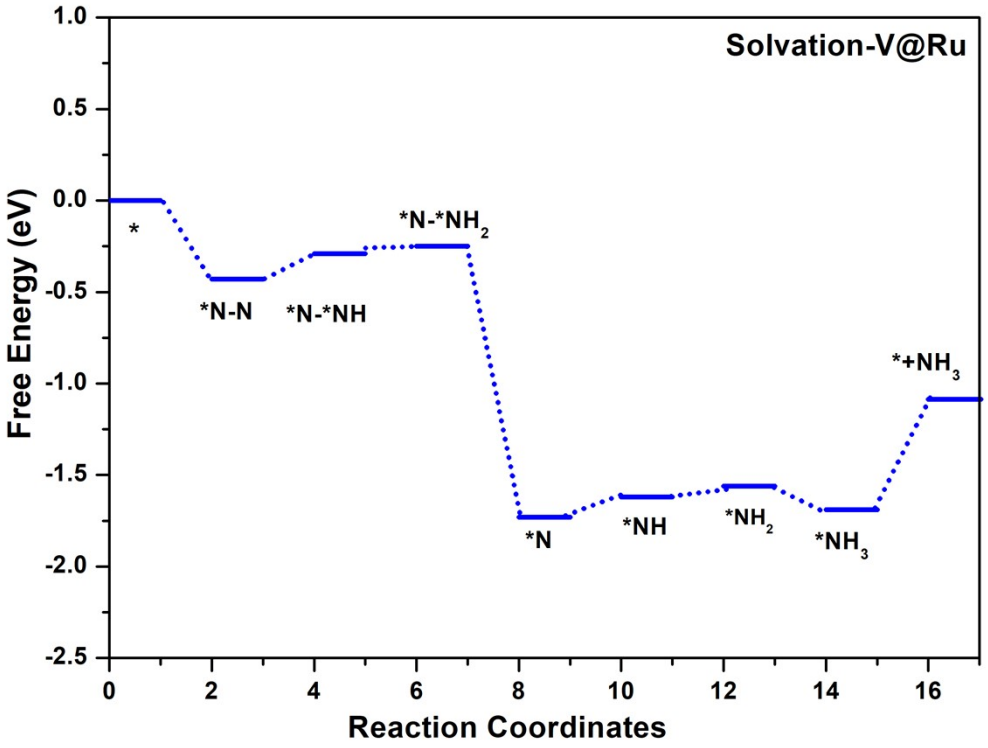

Figure S4: The free energy diagram for V@Ru(0001) together with the solvent effects.

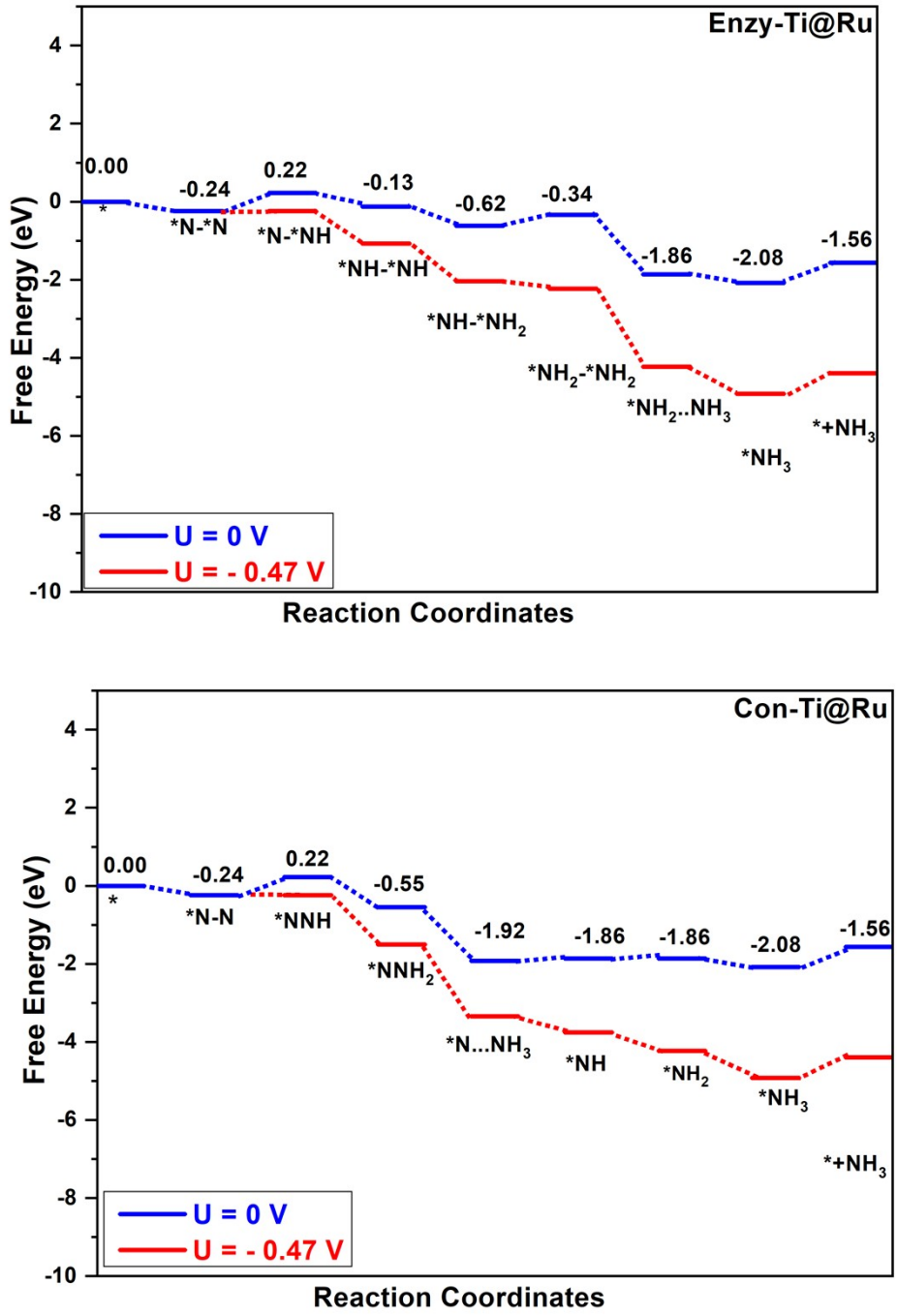

Figure S5: Free energy diagram for enzymatic and consecutive pathway for N_2 reduction to NH_3 using Ti@Ru(0001), at the bottom are various structures of reactive intermediates formed during the reduction process.

Table S3: Gives the kinetic barrier for each of the elementary step during the consecutive reduction pathway for V@Ru(0001)

Elementary steps (Consecutive)	Energy barrier(eV)
*N-N ⟶ *N-*NH	1.14
*N-*NH ⟶ *N-*NH_2	0.85
N-NH_2 ⟶ *N	0.86
*N ⟶ *NH	1.31
*NH ⟶ *NH_2	0.90
*NH_2 ⟶ *NH_3	1.18

Table S4: Gives the kinetic barrier for each of the elementary step during the enzymatic reduction pathway for V@Ru(0001).

Elementary steps (Enzymatic)	Energy barrier (eV)
*N-N ⟶ *N-*NH	1.14
*N-*NH ⟶ *NH-*NH	0.87
*NH-*NH ⟶ *NH-*NH_2	0.72
NH-NH_2 ⟶ *NH_2-*NH_2	1.51
NH_2-NH_2 ⟶ *NH_2	0.43
*NH_2 ⟶ *NH_3	1.19

Table S5: Gives the kinetic barrier for each of the elementary step during the consecutive reduction pathway for Ti@Ru(0001)

Elementary steps (Consecutive)	Energy barrier(eV)
*N-N ⟶ *N-*NH	1.48
*N-*NH ⟶ *N-*NH_2	0.75
N-NH_2 ⟶ *N	0.25
*N ⟶ *NH	1.19
*NH ⟶ *NH_2	0.87
*NH_2 ⟶ *NH_3	1.27

Table S6: Gives the kinetic barrier for each of the elementary step during the enzymatic reduction pathway for Ti@Ru(0001).

Elementary steps (Enzymatic)	Energy barrier (eV)
*N-N ⟶ *N-*NH	1.48
*N-*NH ⟶ *NH-*NH	1.28
*NH-*NH ⟶ *NH-*NH_2	1.09
NH-NH_2 ⟶ *NH_2-*NH_2	0.84
NH_2-NH_2 ⟶ *NH_2	0.22
*NH_2 ⟶ *NH_3	1.27